GEOGRAPHIC VARIATION IN THE LEAF ESSENTIAL OILS OF *HESPEROCYPARIS ARIZONICA* AND *H. GLABRA*

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ABSTRACT

The leaf essential oils were analyzed from four *Hesperocyparis* (=*Cupressus*) *arizonica* and five *H. glabra* populations. The leaf oil of *H. arizonica* has large amounts of umbellulone (18.8%), terpinen-4-ol (11.0%), nezukol (11.6%), limonene (6.6%) and β-phellandrene (6.6%) with moderate amounts of α-pinene (4.1%), sabinene (5.3%) and isophyllocladene (3.1%). The oil of *H. glabra* is dominated by cis-muurola-4(14),5-diene (14.3%), umbellulone (9.3%), α-pinene (8.1%), with moderate amounts of limonene (5.6%), β-phellandrene (5.5%), cis-muurola-3,5-diene (5.3%), cis-muurol-5-en-4-one (4.8%), sabinene (4.0%), epi-zonarene (4.0%) and α-acorenol (3.0%). The concentrations of a number of compounds separate *H. arizonica* and *H. glabra*: umbellulone, terpinen-4-ol, 2-ethyl-isomenthone, cis-muurola-3,5-diene, cis-muurola-4(14),5-diene, epi-zonarene, α-alaskene, γ-cadinene, trans-calamenene, δ-cadinene, italicene ether, cis-muurola-5-en-4-α-ol, cis-muurola-5-en-4-α-ol, 3-oxobutyl-isomenthone, α-acorenol, β-acorenol, cadalene, cis-14-nor-muurol-5-en-4-one, oplopanonyl acetate, isohibaene, isophyllocladene, manoyl oxide, kaur-16-ene and nezukol. Two chemotypes were found in *H. arizonica*: low and high in muurola type compounds. These analyses support the continued recognition of these taxa at the specific level. *Phytologia 92(3): 366-387 (December 1, 2010).*

KEY WORDS: *Hesperocyparis* (=*Cupressus*) *arizonica*, *H. glabra*, terpenoids, geographic variation, taxonomy.

In the latest nomenclature of the cypresses, Bartel and Price in Adams et al. (2009) described a new genus, *Hesperocyparis*, for the Western Hemisphere cypresses (exclusive of *Xanthocyparis vietnamensis* and *Callitropsis nootkatensis*) and Bartel made the new combinations of *Hesperocyparis arizonica* (Greene) Bartel and *H. glabra* (Sudw.) Bartel. Analyses using RAPDs fingerprinting (Bartel et al., 2003) showed *H. glabra* to be distinct from *H. arizonica* (Fig. 1).

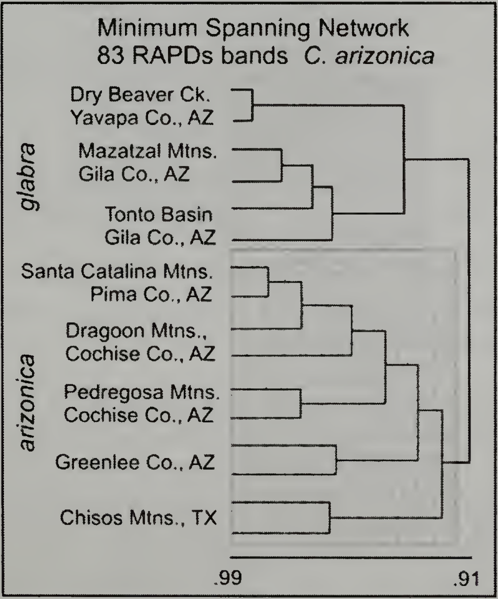

Figure 1. Minimum spanning network (from Bartel et al., 2003).

Contouring the RAPDs clustering of the populations revealed the geographic disjunction between *H. arizonica* and *H. glabra* (Fig. 2).

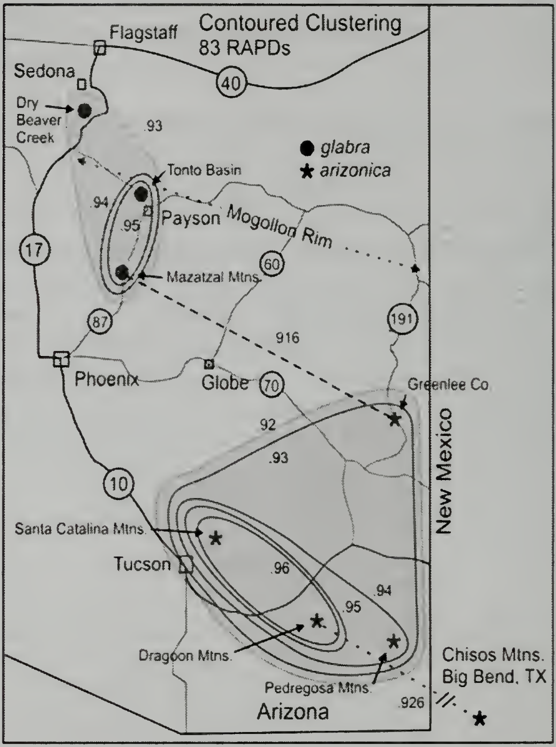

Figure 2. Contoured clustering of populations of *H. arizonica* and *H. glabra* based on 83 RAPDs bands.

The distributions (based on Bartel, 1993) of *H. arizonica* and *H. glabra* are shown in figure 3. Notice the taxa appear to be allopatric except for the new putative population of *H. arizonica* near Prescott. The Prescott collection, if proven to be *H. arizonica,* would be a nearly 200-mile range extension for the species and a significant departure from what was believed to be contrasting habitats and ranges for the two Arizona species. According to Brown's (1982) map of Biogeographic Provinces (BP) of the Southwest, *H. glabra* is restricted to the Interior (Arizonan) BP (which is largely below the Mogollon

Rim), while *H. arizonica* is found within the "Sky Islands" of the Madrean BP. The Madrean BP, which occurs throughout much of north-central Mexico, only enters the US in southeastern Arizona and extreme southwestern New Mexico. Wolf (1948), Schoenike et al. (1975), Little (2005), Rehfeldt (1997) and other authors have all concluded that *H. arizonica* does not range north of Greenlee County nor west of Pima County.

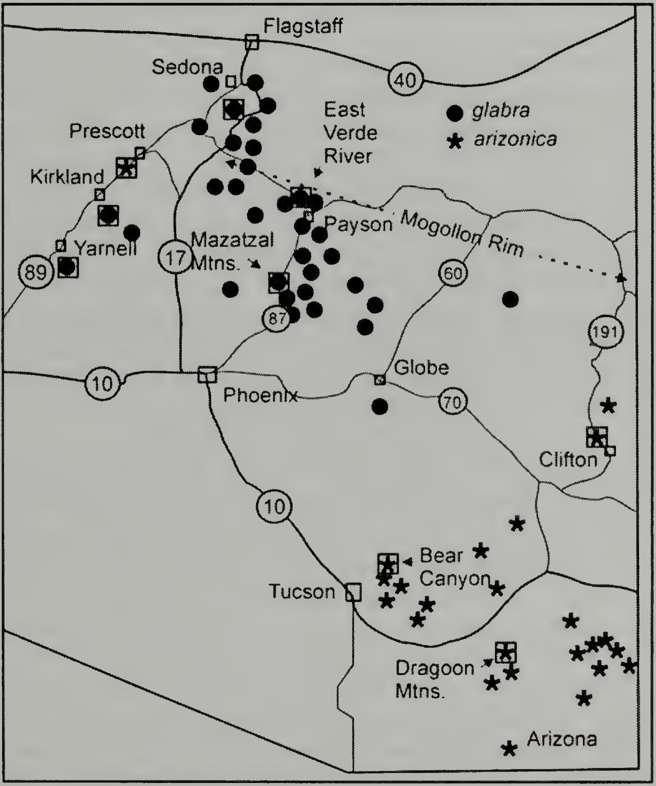

Figure 3. The distributions of the *H. arizonica and H. glabra* (modified from Bartel, 1993). The populations of sampled in this study shown with a box around the symbol.

The leaf essential oil of *H. arizonica* (*C. arizonica*) has been very widely analyzed and reported from mostly cultivated plants (see Emami et al. 2010, for a recent review).

This paper presents the leaf oil compositions and analyses of geographical variation of *H. arizonica* and *H. glabra*.

MATERIALS AND METHODS

Five trees were sampled from four *H. arizonica* and five *H. glabra* populations from locations shown in Figure 3. Collection site information for samples utilized in this study: *Hesperocyparis arizonica*: *Adams 11665-11669*. upper Bear Canyon, 11.8 mi n of Houghton Rd along Catalina Hwy, N 32° 21.801', W 110° 42.765', 1695m, Santa Catalina Mtns., Pima Co., AZ; *Adams 11670-11674*, n side of US191 in dry creek bed, 13 mi. n of Clifton. N 33° 08.057', W 109° 22.608', 1680m, Greenlee Co., AZ, *Adams 11675-11679*, Stronghold Canyon East, 8.5 mi w of US 191, along Ironwood Rd., N 31° 55.540', W 109° 58.007', 1501m, Dragoon Mtns., Cochise Co., AZ; *Adams 12078-12082*, *12301-12310*, 10 mi. sw of Prescott, on Hwy 89, N 34° 27.285', W 112° 32.363', 1657m, Yavapai Co., AZ.

Hesperocyparis glabra, *Adams 11680-11684*, upper Slate Creek, 7.1 mi sw of SR 188, along SR87, N 33° 57.472', W 111° 24.419', 1014m, Mazatzal Mtns., Gila Co., AZ, *Adams 11686-11689*, se of Tonto Natural Bridge St. Park, along SR87, nw of East Verde River, N 34° 18.976', W 111° 23.217', 1475m, Gila Co., AZ, *Adams 11690-11694*, upper Dry Beaver Creek, 0.1 mi. e of SR 179 along Wild Horse Mesa Rd., N 34° 46.131', W 111° 45.779', 1197m, Yavapai Co., AZ, *Adams 12073-12077*, 11 mi. se of Kirkland Jct., Milk Creek, above road crossing, N 34° 18.029', W 112° 29.7096', 1193m, Yavapai Co., AZ, *Adams 12083-12087*, 6 mi. se of Yarnell, AZ, southern Weaver Mtns., N 34° 10.450', W 112° 39.139, 1364m, Yavapai Co., AZ. All specimens are deposited in the BAYLU herbarium.

Isolation of Oils - Fresh leaves (200 g) were steam distilled for 2 h using a circulatory Clevenger-type apparatus (Adams, 1991). The oil samples were concentrated (ether trap removed) with nitrogen and the samples stored at -20°C until analyzed. The extracted leaves were oven dried (100°C, 48 h) for determination of oil yields.

Chemical Analyses - Oils from 10-15 trees of each of the taxa were analyzed and average values reported. The oils were analyzed on a HP5971 MSD mass spectrometer, scan time 1 sec., directly coupled to a HP 5890 gas chromatograph, using a J & W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column (see 5 for operating details). Identifications were made by library searches of our volatile oil library (Adams, 2007), using the HP Chemstation library search routines, coupled with retention time data of authentic reference compounds. Quantitation was by FID on an HP 5890 gas chromatograph using a J & W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column using the HP Chemstation software.

Data Analysis - Terpenoids (as per cent total oil) were coded and compared among the species by the Gower metric (1971). Principal coordinate analysis was performed by factoring the associational matrix using the formulation of Gower (1966) and Veldman (1967).

RESULTS AND DISCUSSION

Table 1 shows the composition of average values of *H. arizonica* and *H. glabra,* as well as some plants with unusual oils. The leaf oil of *H. arizonica* has large amounts of umbellulone (18.8%), terpinen-4-ol (11.0%), nezukol (11.6%), limonene (6.6%) and β-phellandrene (6.6%) with moderate amounts of α-pinene (4.1%), sabinene (5.3%) and isophyllocladene (3.1%). The oil of *H. glabra* is dominated by cis-muurola-4(14),5-diene (14.3%), umbellulone (9.3%), α-pinene (8.1%), with moderate amounts of limonene (5.6%), β-phellandrene (5.5%), cis-muurola-3,5-diene (5.3%), cis-muurol-5-en-4-one (4.8%), sabinene (4.0%), epi-zonarene (4.0%) and α-acorenol (3.0%). The concentrations of a number of compounds separate *H. arizonica* and *H. glabra* (Table 1). Particularly useful are umbellulone, terpinen-4-ol, 2-ethyl-isomenthone, cis-muurola-3,5-diene, cis-muurola-4(14),5-diene, epi-zonarene, α-alaskene, γ-cadinene, trans-calamenene, δ-cadinene, italicene ether, cis-muurola-5-en-4-α-ol, cis-muurola-5-en-4-α-ol, 3-oxobutyl-isomenthone, α-acorenol, β-acorenol, cadalene, cis-14-nor-muurol-5-en-4-one, oplopanonyl acetate, isohibaene, isophyllocladene, manoyl oxide, kaur-16-ene and nezukol.

The presence of the murrol family of compounds seems characteristic of *H. glabra* (as opposed to *H. arizonica*). It now appears that samples ascribed to *H. arizonica* (*C. arizonica*) by Adams et al. (1997) were actually *H. glabra*. Likewise, Emami et al. (2010) reported that the leaf oil of *C. arizonica* cultivated in Iran contained all of the muurol components found in *H. glabra*. It seems likely that many or most of the reports on the oil of Arizona cypress cultivated around the world are actually based on *H. glabra*. This observation corroborates Wolf's (1948) assertion that most of the trees cultivated around the world as Arizona cypress are *H. glabra* grown from seed originally collected from the Rye Creek area of Gila County. Incorrectly identified as *Cupressus arizonica* since its introduction into England as early as 1888 (Peattie, 1953), many if not all named Arizona cypress cultivars are derived from *H. glabra* (Jacobson, 1996). Similarly, Posey and Goggans (1967) concluded that the Arizona cypress grown as Christmas trees in the southeastern US likely came from a few individual *H. glabra* trees.

To better visualize the variation among individuals, 63 terpenoids were used to compute similarities among the 46 plant oils and the matrix was factored. This produced eigenroots that accounted for 38.2%, 5.5%, 4.5%, 4.2% and 3.6% of the variance among 46 individuals. Clearly, most of the variance was in the first eigenroot, implying two groups among the data set. A Principal Coordinates Ordination (PCO) divides the 46 individuals into *H. arizonica* and *H. glabra* (Fig. 4). Notice some variation among the *H. glabra* individuals with 2 plants from the Mazatzal Mtns. population loosely clustering, as well as the plants from the Yarnell population.

Based on the position of M1 (11680) on the PCO (Fig. 4), one might suspect that it might be introgressed by *H. arizonica*. However, a close examination of the oil composition (Table 1) reveals that M1 does not contain compounds characteristic of *H. arizonica*, but instead, M1 has very unusual amounts of some compounds (sabinene, limonene, β-phellandrene, citronellol). Moreover, M1 contains the typical muurol components of *H. glabra*.

The oils of the plants in Yarnell population cluster high on axis 3 (Fig. 4). The leaf oil composition of the most extreme plant (Y3, 12085) is shown in Table 1. Y3 is in contrast to M1 in having very low amounts of sabinene, limonene, β-phellandrene but a large amount of nezukol (14.8%) as well as the typical murrol constituents. However, it also contains some components typical of *H. arizonica*: isohibaene and 13-epi-manoyl oxide.

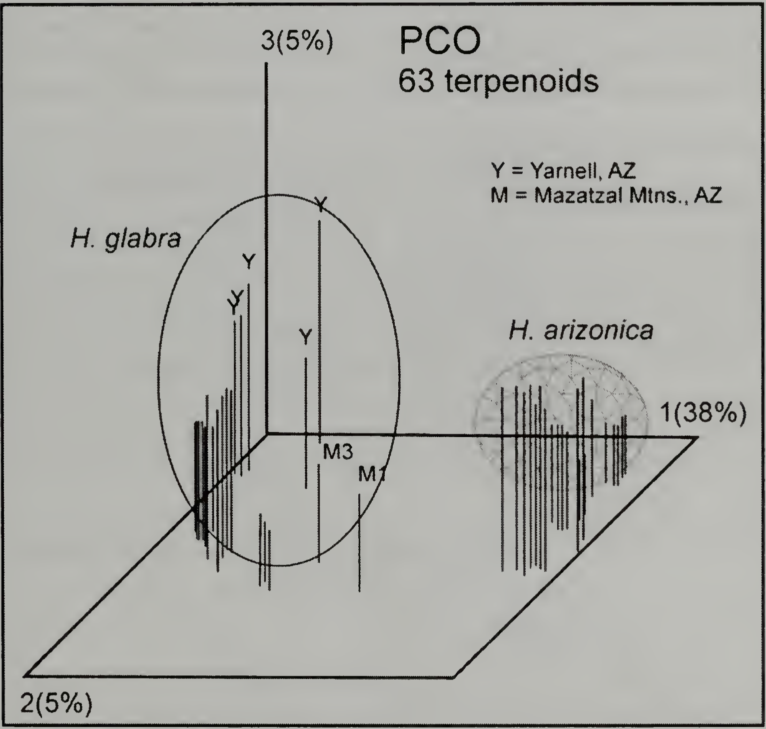

Figure 4. PCO based on 63 terpenoids shows the two major groups: *H. arizonica* and *H. glabra*. M1 (11680) and M3 (11682) are from the Mazatzal Mtns. population and those labeled Y are from the Yarnell population.

Factoring the matrix of the *H. arizonica* similarities resulted in three eigenroots that appear to be biologically significant. These eigenroots accounted for 16%, 12% and 8% of the variance among the 25 samples. Ordination reveals (Fig. 5) that both the Dragoon Mtns. and Prescott populations are di-morphic with individuals that have the muurola related compounds (cis-muurola-3,5-diene, cis-muurola-4(14),5-diene, epi-zonarene, trans-calamenene, cis-muurola-5-en-4-α-ol, cis-muurola-5-en-4-α-ol, and cis-14-nor-muurol-5-en-4-one). This is also seen in table 1 by comparing the *H. arizonica* (ariz) average values with D3 (Dragoon Mtns., *Adams 11677*) and Prescott P2 (*Adams 12079*). In fact, the most similar oil to P2 is D3. Whereas only 2 of 10 trees in the Prescott population had the muurola suite, 3 of 5 trees in

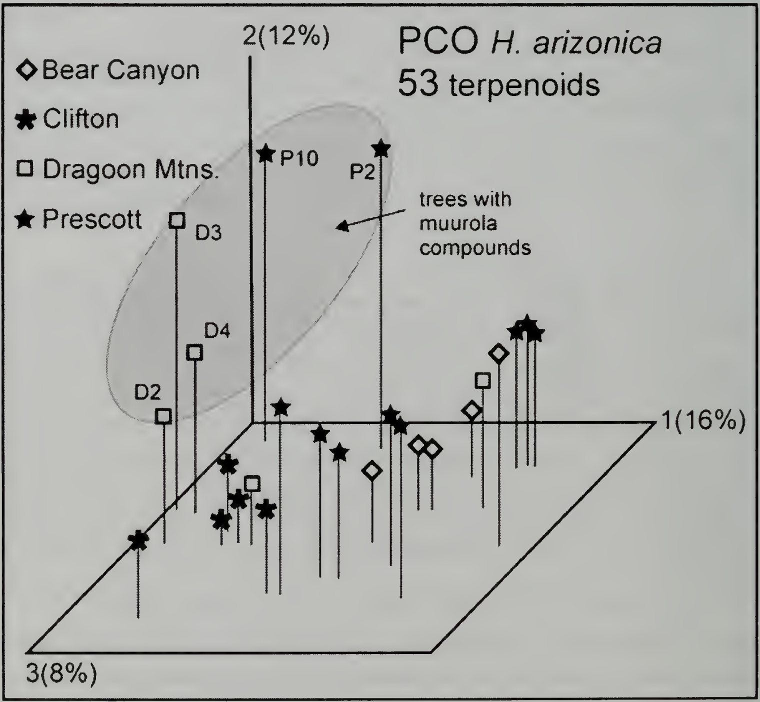

Figure 5. PCO based on 53 terpenoids of *H. arizonica* based on leaf oils. Note the Dragoon Mtns. and Prescott populations are di-morphic for the muurola compounds.

the Dragoon Mtns. had the muurola suite of compounds but the other two trees had absolutely no traces of the muurola compounds. In general, the muurola compounds were found in trace values in two trees from the Bear Canyon and two trees from the Clifton populations. The genes for the muurola pathway seem to be widespread in *H. arizonica*. The muurola compounds are characteristically in large concentrations in *H. glabra*. The presence of the muurola genes in some *H. arizonica* trees could be explained by past hybridization or relictual ancestral lineage sorting between H. arizonica and H. glabra. The lack of the occurrence of other components of *H. glabra* in any *H. arizonica* plants sampled suggests that hybridization is not occurring at present and favors the relictual ancestral lineage sorting hypothesis.

The discovery of *H. arizonica* near Prescott, outside its historical range and in a very xeric habitat compared to the more mesic habitats in southeastern Arizona is difficult to explain if the stand were natural. The grove near Prescott is very small and consists of only 10 trees larger than 1" DBH plus a few seedlings. As cis-muurola-4(14),5-diene is a characteristic component of the muurola suite, it is used to illustrate the diversity in Table 2. We have identified 3 age classes in the grove (approximated by DBH: 20-22", 5.6-11.1", seedlings - 1.6",Table 2). The two trees highest in cis-muurola-4(14),5-diene (and other muurola components) are P2 (18" DBH) and P10 (1"DBH). Recall that P2 and is most similar in its oils to D3 from the Dragoon

Table 2. Analyses of the 10 largest trees from the Prescott population (DBH>1"). % CM45 = % cis-muurola-4(14),5-diene.

Tree #	Rings	Size (DBH)	% CM45
P1	33-40	11.1"	0.3
P2	63-70	20.4"	3.5
P3		21-22"(3 trunks)	0.1
P4	30-44	6.4"	0.2
P5		5.6"	0.05
P6		21.3"	0.0
P7		2.1"	0.05
P8		1.6"	0.05
P9		7.5"	0.0
P10		0.5"	3.8

Mtns. Most of the trees contain small or trace amounts of cis-muurola-4(14),5-diene (Table 2). A spatial analysis of these 10 trees is shown in Fig. 6.

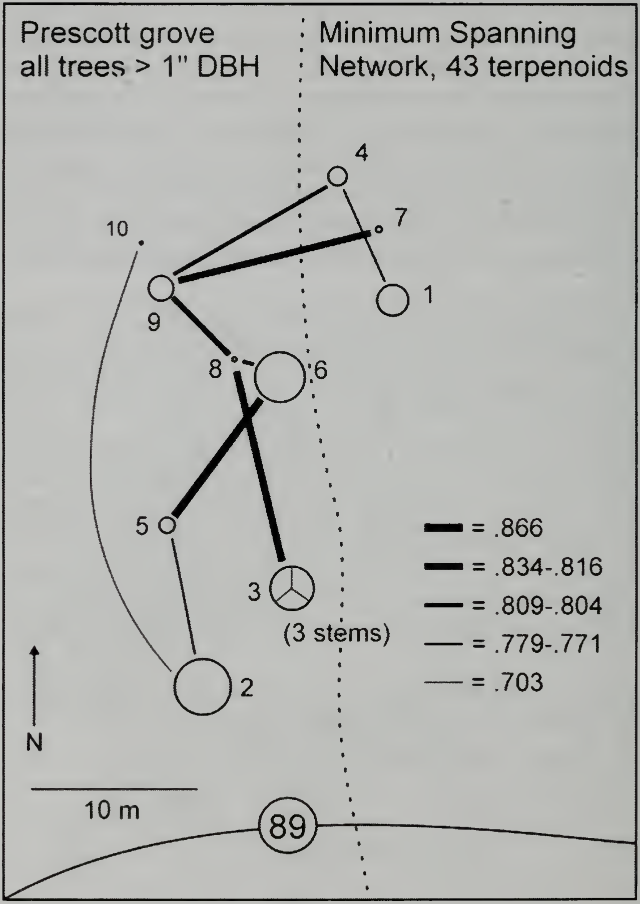

Figure 6. Minimum spanning network (based on 43 terpenoids) for the 10 largest trees in the Prescott grove. The size of the circles is proportional to the DBH (tree 2 = 18" DBH, tree 10 = 1" DBH). Highway 89 is noted by the circled number.

Although trees P2 and P10 share the muurola suite of components, their oils are the least similar of the 10 trees (Fig. 6). Based on field observations in this area, the population appears to have been founded by 3 trees (P2, P3, P6, Fig. 6). Both trees P2 and P3 have dead tops and are declining in health. No additional cypress trees were found in a survey of the ravine above and below this population. There is some litter and topsoil under the trees and new seedlings have been established under the canopy of the large, older trees. No seedlings were seen in the more xeric slopes outside the canopy of the older trees. Growth rings are not very useful due to droughts (no ring that year) and multiple monsoon events (multiple rings/ year). However, coring 3 trees in the population (Table 2) gave a range of ages of 63 - 70 years for the largest tree (#2). If 70 years were true, that would put the origin around 1940. Even allowing for a 50% error (70+35 = 105), that would put the origin at 1905. Historical records record that this section of US Highway 89 was known (and still is) as the White Spar Road. The White Spar Mine (Barite) was located south of the cypress grove in 1880 with claims patented in 1904. In 1927, the White Spar Road became part of US Highway 89. Because *H. arizonica* trees in the Dragoon Mtns. are easily accessible and cones are easily collected, *H. arizonica* could have been brought to the Prescott area in the 20th century.

In light of the above discussion, the Prescott population appears to be an anthropogenic introduction. This conclusion should not be unexpected given that both Arizona cypresses, *H. arizonica* and particularly, *H. glabra*, are very commonly cultivated in Arizona outside their respective native ranges was well as elsewhere throughout the United States and the world. Identified generically in the horticultural community as "Arizona Cypress", both species are used as ornamentals, windbreak trees and sometimes on disturbed sites for erosion control (Sullivan, 1993). While *H. glabra* has been cultivated to a greater degree given its comparative better hardiness and desirability as a Christmas tree (Jacobson, 1996), both species have been cultivated for more than a century; *H. arizonica* since at least 1882 (Dallimore and Jackson, 1966) and *H. glabra* since as early as 1888 (Peattie, 1953). Interestingly, *H. glabra* was in cultivation prior to its description in 1907, which may have contributed to the confusion of the two species in cultivation.

To examine infraspecific variation in *H. glabra*, the terpenoids similarity matrix was factored. The first three eigenroots accounted for 16.6%, 10.9% and 8.8% of the variance among the 26 samples. Ordination revealed that the unusual nature of two of the Mazatzal Mtns. plants and the divergence of the Yarnell population (Fig. 7). The Kirkland, Sedona and East Verde River populations are interspersed in the ordination (Fig. 7). It should be noted that one of the Yarnell plants and three of the Mazatzal Mtns. plants are interspersed with typical *H. glabra* (Fig. 7). All of these five populations are relatively near (15-60 mi.), so pollen flow is possible.

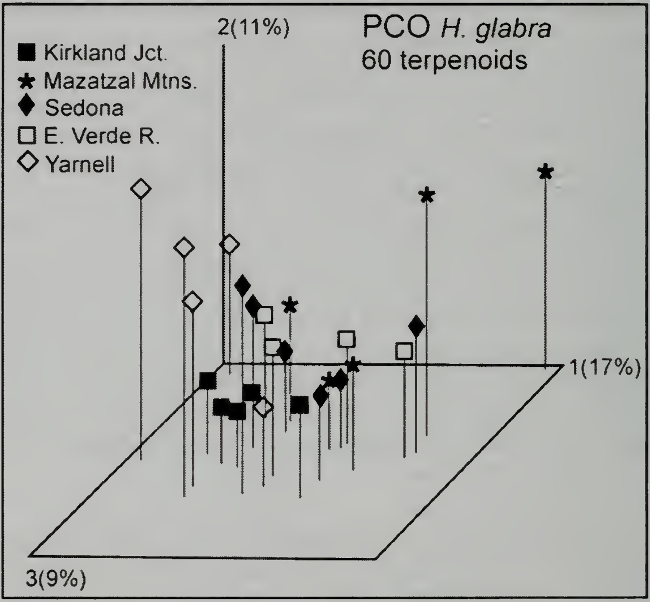

Figure 7. PCO of *H. glabra* individuals based on 60 terpenoids.

CONCLUSIONS

Two chemotypes were found in *H. arizonica*: low muurola trees (typical of the species) and a few high murrola trees. A disjunct, population near Prescott has both chemotypes as also found in the Dragoon Mtns. population. The leaf oil of one of the Prescott 'high muurol' chemotype individuals (P2) was found to be most similar to a tree from the Dragoon Mtns., indicating that the Prescott genotypes came from southeastern Arizona. The Prescott *H. arizonica* population appears to have been introduced by man with germplasm (seed cones) from the Dragoon Mtns. or an adjacent area. The unusual amount of variation found in the Prescott (*H. arizonica*) and Yarnell (*H. glabra*) populations is puzzling and deserves additional study.

ACKNOWLEDGEMENTS

Thanks to Tonya Yanke for lab assistance. This research was supported in part with funds from Baylor University.

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Table 1. Leaf essential oil compositions for *H. arizonica* (ariz), *H. glabra* (glab), and putative introgressant from Prescott (12079,P2) and unusual oils from plants from the Mazatzal Mtns. (11680, M1) and Yarnell (12085, Y3). Compounds with an asterisk (*) were used in numerical analysis. Compounds in bold show large differences between the taxa. F (from ANOVA) * = 0.05; ** = 0.01; ***= 0.001.

RT	compound	ariz	glab	F	D3	P2	M1	Y3
846	(E)-2-hexenal	0.4	0.3	ns	t	-	0.5	0.2
921	tricyclene	0.1	0.1	ns	t	t	t	t
924	**α-thujene***	**0.9**	**0.6**	**36*** **	**1.8**	**1.3**	**1.1**	**0.1**
932	**α-pinene***	**3.9**	**12.6**	**14*** **	**3.5**	**7.7**	**10.6**	**8.7**
945	α-fenchene	-	0.1	ns	-	-	0.1	0.1
946	camphene	t	0.2	ns	t	t	0.1	0.1
953	thuja-2,4-diene	-	t	nt	-	-	-	0.1
969	sabinene*	4.3	3.4	ns	8.2	6.1	9.6	1.1
974	β-pinene*	0.2	0.4	nt	0.2	0.3	0.4	0.4
988	myrcene*	1.7	1.7	6.9*	2.3	2.9	3.9	0.8
994	2-octanol	t	t	nt	-	-	-	-
1002	α-phellandrene	0.1	0.2	ns	0.2	0.2	0.2	t
1008	δ-3-carene*	0.3	1.8	ns	0.1	0.1	1.1	0.9
1014	**α-terpinene***	**1.4**	**0.7**	**168*** **	**1.9**	**1.4**	**1.3**	**0.2**
1020	p-cymene*	1.1	0.7	28***	2.0	1.5	1.0	0.4
1024	limonene*	4.2	4.0	ns	5.9	6.1	15.3	0.7

RT	compound	ariz	glab	F	D3	P2	M1	Y3
1025	β-phellandrene*	4.2	4.0	ns	5.9	6.1	15.3	0.7
1026	1,8-cineole	t	-	nt	-	-	-	-
1038	2-heptyl acetate	t	-	nt		-	-	-
1054	**γ-terpinene***	**1.8**	**1.1**	**119*****	**2.5**	**2.3**	**1.8**	**0.3**
1065	cis-sabinene hydrate*	0.6	0.2	32***	1.0	0.7	0.6	0.1
1086	**terpinolene***	**1.7**	**1.0**	**62*****	**1.7**	**1.6**	**1.7**	**0.5**
1087	2-nonanone	t	-	nt	t	-	-	-
1098	trans-sabinene hydrate*	0.6	0.1	28***	0.8	0.5	0.3	0.1
1099	linalool*	0.3	0.2	nt	0.3	0.4	0.2	t
1100	n-nonanal	t	-	nt	t	-	-	0.2
1112	trans-thujone	t	-	nt	-	-	-	-
1118	**cis-p-menth-2-en-1-ol***	**0.7**	**0.2**	**84*****	**0.9**	**0.5**	**0.3**	**0.1**
1122	α-campholenal	-	0.1	nt	-	-	t	0.1
1136	trans-p-menth-2-en-1-ol*	0.5	0.2	28***	0.6	0.4	0.3	0.5
1141	camphor*	0.6	1.3	ns	0.2	0.3	0.3	0.3
1145	camphene hydrate	0.3	-	nt	0.4	0.3	t	t
1148	citronellal	-	t	nt	-	-	0.2	t
1160	pinocarvone	-	-	nt	-	-	-	0.2
1167	**umbellulone***	**19.0**	**8.8**	**88*****	**22.7**	**15.7**	**3.7**	**3.9**
1174	**terpinen-4-ol***	**5.9**	**2.7**	**76*****	**8.2**	**7.8**	**3.8**	**0.9**

RT	compound	ariz	glab	F	D3	P2	M1	Y3
1179	p-cymen-8-ol*	1.3	0.5	6.4*	1.8	0.8	0.4	0.2
1186	α-terpineol*	0.7	0.5	ns	0.5	0.4	0.2	0.2
1195	cis-piperitol	0.2	-	nt	0.3	-	0.1	0.1
1195	myrtenal	-	0.1	nt	-	-	0.1	-
1198	shisofuran	0.2	-	nt	0.2	0.2	-	-
1205	trans-piperitol	0.3	0.3	nt	0.3	0.2	-	-
1206	verbenone	-	0.2	nt	-	-	-	-
1215	trans-carveol	t	-	nt	-	-	-	-
1223	citronellol*	0.1	2.4	18**	t	0.1	3.6	0.1
1232	thymol, methyl ether	0.1	t	nt	-	0.5	0.2	0.3
1239	carvone	t	t	nt	t	-	0.1	0.3
1241	carvacrol, methyl ether	t	-	nt	-	0.1	-	-
1249	piperitone	0.2	t	nt	t	0.2	0.1	t
1254	linalool acetate	0.1	-	nt	-	0.1	-	-
1287	bornyl acetate	0.1	-	nt	0.6	0.1	-	-
1289	thymol	0.2	t	nt	t	0.1	t	0.2
1293	**2-ethyl-isomenthone***	-	**0.2**	**49*****	-	-	**0.1**	**0.9**
1299	terpinen-4-yl acetate*	0.9	0.5	19**	1.3	1.3	0.5	0.5
1315	(2E,4E)-decadienal	t	-	nt	-	-	-	-
1319	(2E,4E)-decadienol	t	-	nt	-	-	-	-

RT	compound	ariz	glab	F	D3	P2	M1	Y3
1339	trans-carvyl acetate	-	t	nt	t	-	0.1	-
1346	**α-terpinyl acetate***	**2.6**	**0.6**	**139*****	**3.0**	**4.2**	**0.7**	**0.2**
1373	α-copaene	t	-	nt	-	-	-	-
1410	α-cedrene*	-	0.5	nt	-	-	-	0.3
1419	β-cedrene*	-	0.3	nt	-	-	-	0.5
1444	bakerol	-	-	nt	-	-	-	0.2
1448	**cis-muurola-3,5-diene***	**0.2**	**4.3**	**79*****	**1.7**	**1.5**	**2.0**	**3.2**
1452	α-humulene	-	t	nt	-	-	-	0.2
1465	**cis-muurola-4(14),5-diene***	**0.5**	**11.8**	**80*****	**4.0**	**3.5**	**5.0**	**8.0**
1479	ar-curcumene	-	-	nt	-	-	t	0.2
1482	citronellol isobutyrate	-	0.2	nt	-	-	0.1	-
1499	β-macrocarpene	-	-	nt	-	-	-	0.2
1500	α-muurolene	0.1	-	nt	-	-	-	-
1501	**epi-zonarene***	**t**	**3.9**	**80*****	**1.0**	**0.9**	**1.4**	**2.1**
1504	cuparene	-	-	nt	-	-	-	0.2
1512	**α-alaskene***	**-**	**0.2**	**nt**	**-**	**-**	**t**	**0.3**
1513	**γ-cadinene**	**0.2**	**-**	nt	-	-	-	-
1518	endo-1-bourbonanol	t	-	nt	-	-	-	t
1521	**trans-calamenene***	**t**	**2.7**	**84*****	**0.2**	**0.1**	**0.6**	**3.9**
1522	**δ-cadinene***	**0.8**	**t**	**12****	**0.2**	**0.1**	**t**	**-**

RT	compound	ariz	glab	F	D3	P2	M1	Y3
1533	**10-epi-cubebol***	**-**	**0.4**	**43*****	**-**	**-**	**t**	**0.2**
1536	**italicene ether***	**-**	**0.9**	**25****	**-**	**0.1**	**0.2**	**1.5**
1537	α-cadinene	t	-	nt	-	-	-	-
1544	α-calacorene	-	0.2	nt	-	-	-	0.2
1548	elemol	0.2	-	nt	0.1	-	-	-
1550	**cis-muurola-5-en-4-β-ol***	**0.1**	**1.6**	**44*****	**0.5**	**0.5**	**1.0**	**0.9**
1559	**cis-muurola-5-en-4-α-ol***	**0.2**	**1.9**	**35*****	**0.7**	**0.7**	**1.2**	**1.2**
1561	**germacrene D-4-ol**	**0.9**	**-**	**19*****	**0.2**	**0.1**	**-**	**-**
1564	β-calacorene	-	0.1	nt	-	-	-	0.1
1582	caryophyllene oxide	-	t	nt	-	-	t	-
1600	**cedrol***	**-**	**1.2**	**41*****	**-**	**t**	**t**	**3.2**
1607	β -oplopenone	0.2	-	nt	t	0.1	-	-
1608	humulene epoxide II	t	0.1	nt	-	-	t	-
1618	**1,10-di-epi-cubenol***	**0.1**	**0.4**	**81*****	**t**	**0.1**	**0.1**	**0.4**
1627	1-epi-cubenol	t	-	nt	t	-	-	-
1627	**3-oxobutyl-isomenthone***	**-**	**0.6**	**nt**	**-**	**-**	**t**	**2.3**
1632	**α-acorenol***	**-**	**3.2**	**61*****	**-**	**-**	**0.2**	**3.8**
1636	**β-acorenol***	**-**	**0.6**	**59*****	**-**	**-**	**t**	**0.8**
1638	epi-α-cadinol*	0.6	0.3	nt	0.1	0.1	0.1	0.3
1638	epi-α-muurolol*	0.6	0.3	nt	0.2	0.1	0.1	0.3

RT	compound	ariz	glab	F	D3	P2	M1	Y3
1644	α-muurolol	0.2	-	nt	-	-	-	-
1645	cubenol	-	t	nt	-	-	-	-
1652	α -cadinol*	1.6	0.9	ns	0.3	0.4	0.2	0.8
1661	**terpenoid,43,139,155,238***	-	**0.6**	**55*** **	-	-	**0.1**	**1.6**
1675	**cadalene***	-	**0.5**	**24*** **	-	-	**0.1**	**1.2**
1685	α-bisabolol	t	-	nt	-	-	-	-
1688	**cis-14-nor-muurol-5-en-4-one***	**0.1**	**4.0**	**46*** **	**0.2**	**0.1**	**0.7**	**9.5**
1740	(E)-isoamyl cinnamate	0.1	-	nt	-	t	-	-
1748	(Z)-isoamyl cinnamate	0.2	-	nt	-	0.1	-	-
1887	**oplopanonyl acetate**	**1.0**	**0.1**	**25****	**0.1**	**0.2**	-	-
1905	isopimara-9(11),15-diene	0.4	-	nt	0.3	0.4	-	0.3
1933	**isohibaene***	**0.9**	**t**	**68*** **	**0.2**	**0.6**	-	**0.3**
1941	sandaracopimara-8(14),15-diene	0.3	-	nt	t	0.2	-	-
1960	iso-sandaracopimara-8(14),15-diene	1.0	t	nt	0.1	-	0.2	0.6
1966	**isophyllocladene***	**3.7**	**0.4**	**36*** **	**1.8**	**4.2**	**t**	**1.0**
1978	manoyl oxide*	2.0	0.8	ns	1.0	1.8	0.7	3.7
1987	**13-epi-manoyl oxide***	**0.5**	**t**	**5.9***	**0.2**	**0.4**	**0.2**	**1.4**

RT	compound	ariz	glab	F	D3	P2	M1	Y3
2034	**kaur-16-ene***	**0.4**	**-**	**nt**	**0.1**	**0.3**	**t**	**-**
2055	abietatriene*	0.2	0.2	nt	-	0.1	0.2	0.3
2087	abietadiene*	0.4	0.9	4.6*	-	t	0.2	0.5
2090	diterpene, 55,41,272,290*	0.4	-	nt	0.1	0.3	-	0.4
2105	isoabienol	0.6	0.1	nt	0.2	-	-	-
2132	**nezukol***	**15.2**	**0.6**	**42*****	**7.1**	**11.0**	**1.6**	**14.8**
2209	phyllocladanol*	1.3	0.5	ns	t	t	-	0.8
2282	sempervirol	0.3	0.1	nt	t	0.5	0.2	0.4
2314	trans-totarol	0.2	0.1	nt	t	0.3	0.2	0.4
2331	trans-ferruginol	0.1	t	nt	t	0.2	t	0.3

AI = Arithmetic Index on DB-5 column. Compositional values less than 0.1% are denoted as traces (t). Unidentified components less than 0.5% are not reported.